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U.S. Department of Energy
Office of Civilian Radioactive Waste Management

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Update on Waste Package Materials Selection, Heat Treatment and Degradation Modes

Presented to:
Nickel Institute Workshop No. 6

Presented by:
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Waste Package Modeling and Testing

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ACKNOWLEDGEMENT

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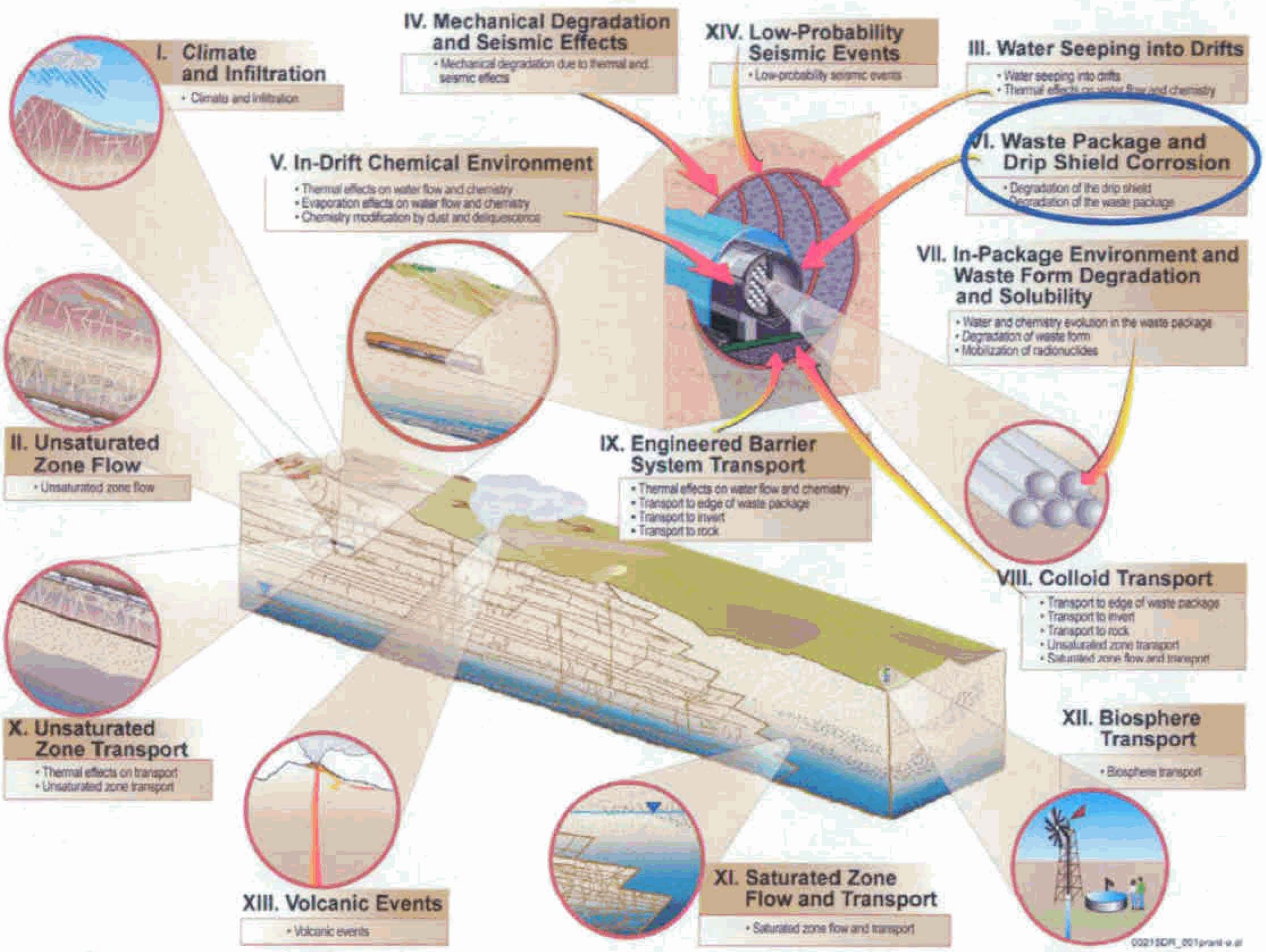
OUTLINE

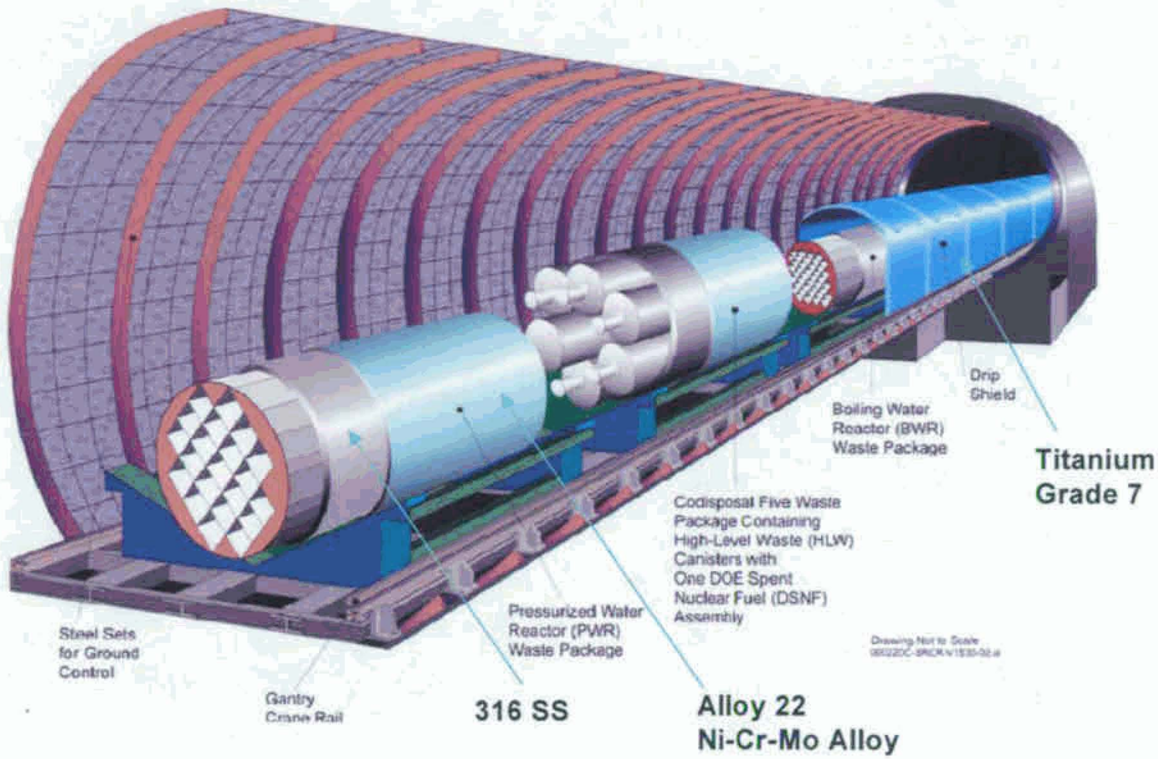
- Waste Package (WP) and Drip Shield (DS) Materials
- In-Drift Environment and Laboratory Testing
- Degradation of Alloy 22
- Conclusions

Overview of Repository Components



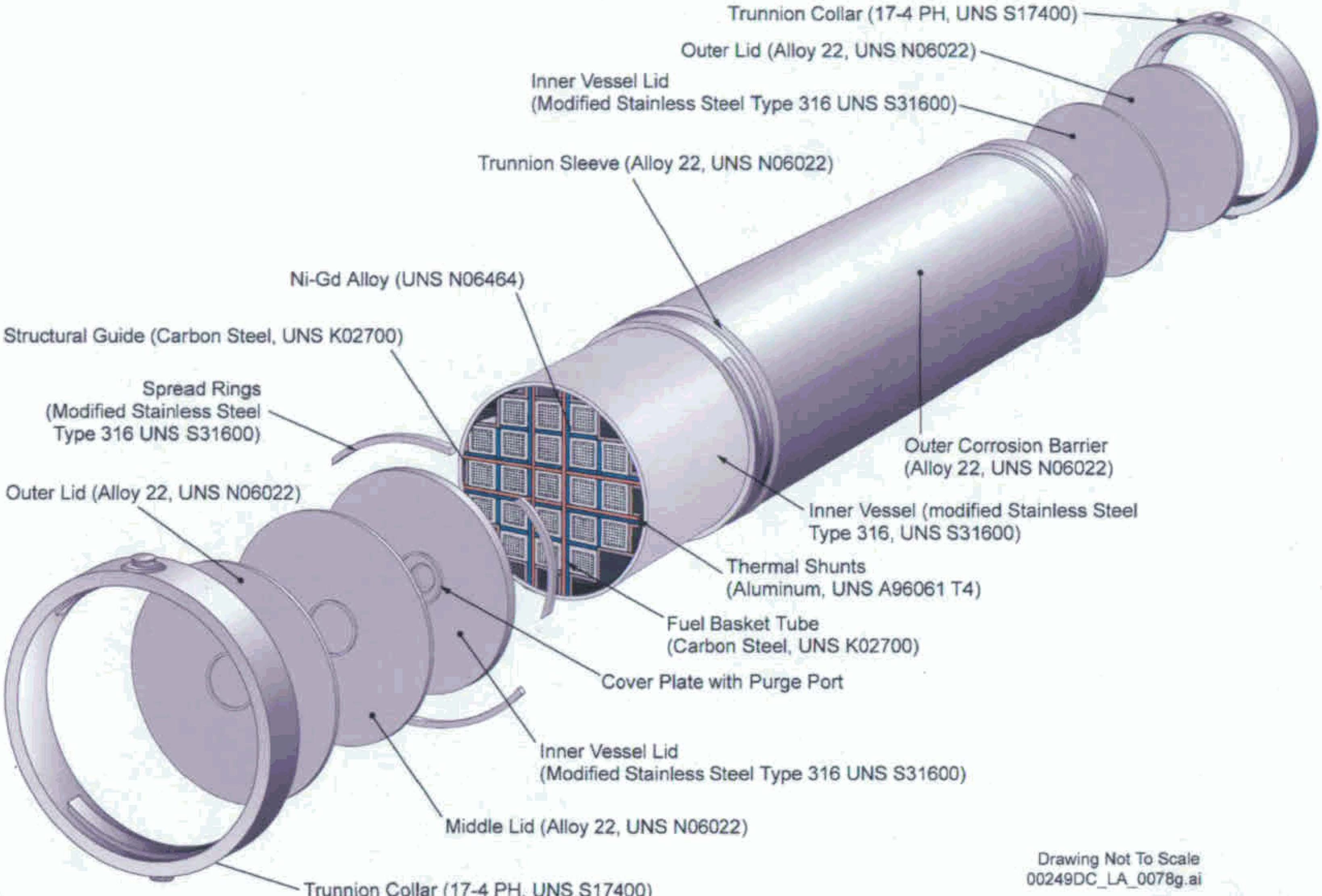
Focus here is on waste package corrosion element of multi-component repository performance assessment model

Emplacement Drifts and Waste Packages



- Outer corrosion resistant barrier: Alloy 22 cylinder
- Inner structural vessel: 316 Stainless Steel cylinder
- Drip shield plates: Ti Grade 7
- Drip shield structural supports: Ti Grade 24/29

Waste Package Materials



Drawing Not To Scale
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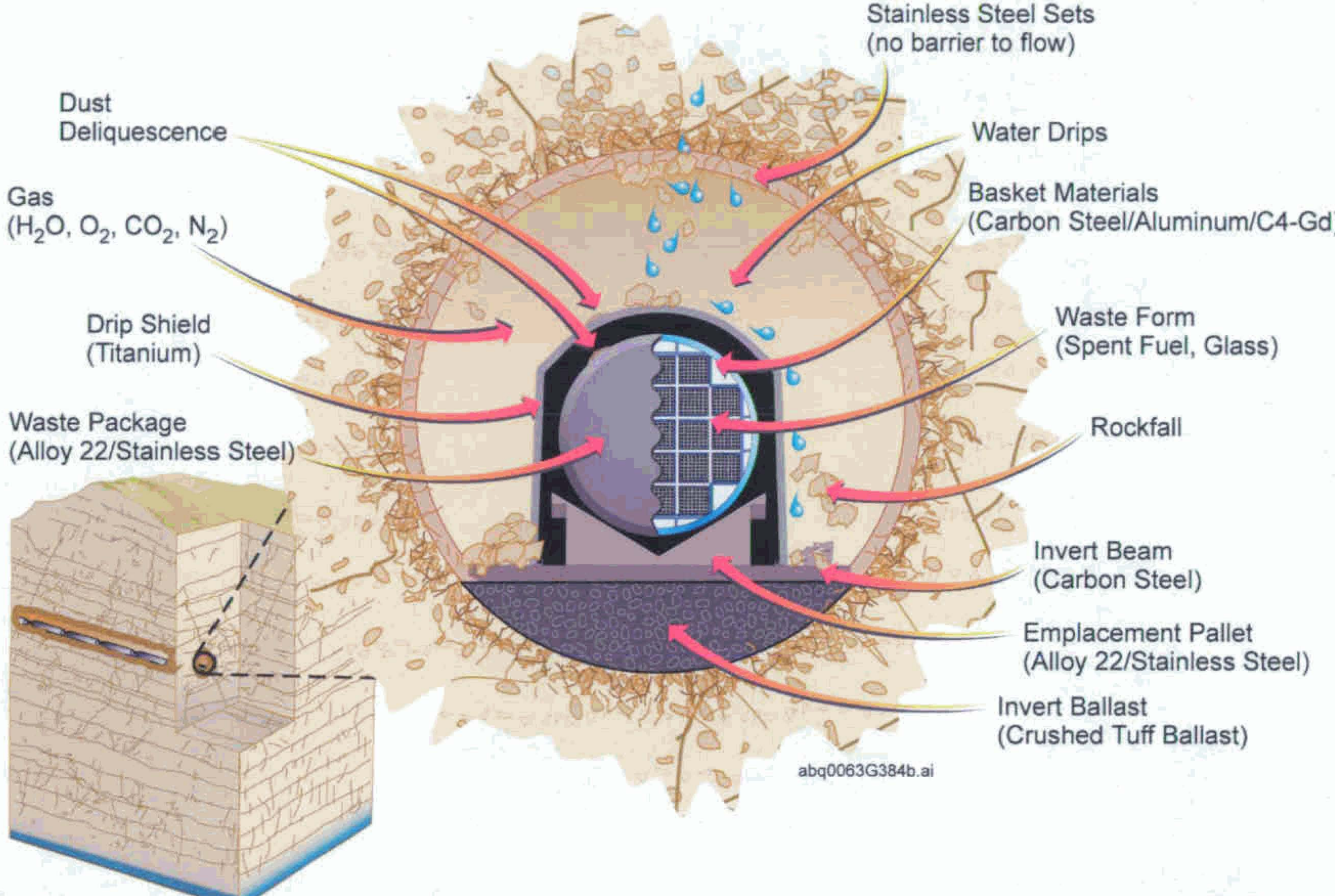
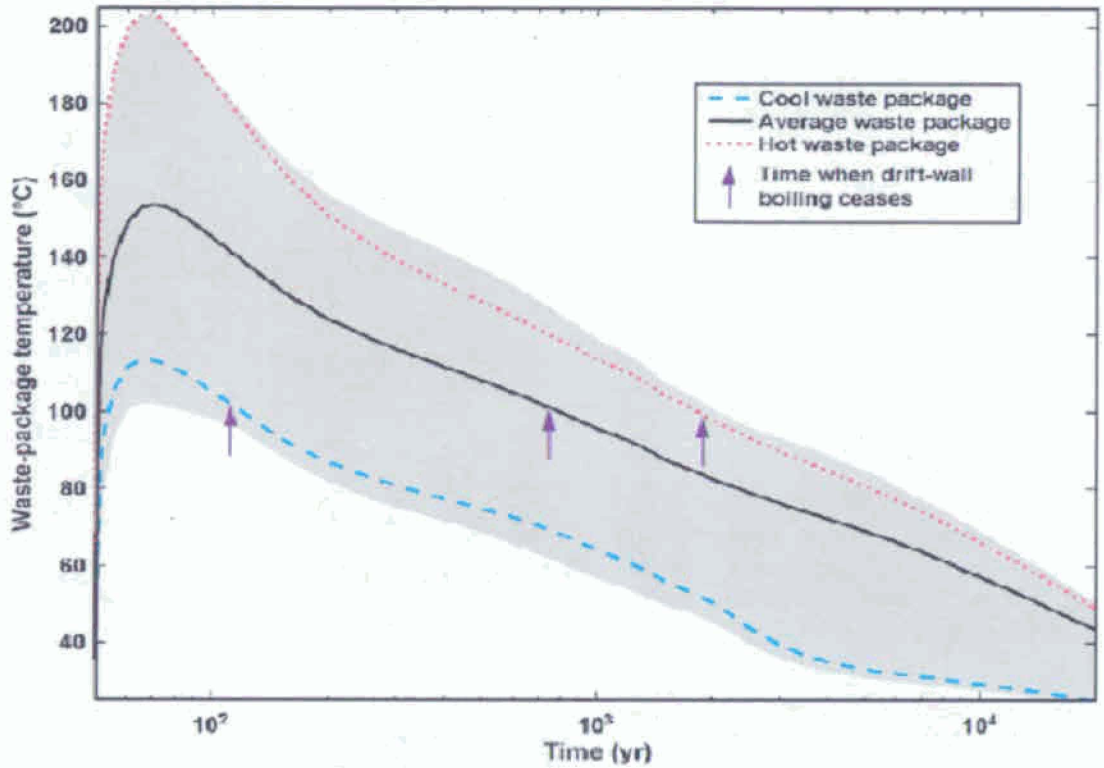
Waste Package and Drip Shield Environments



Waste Package Temperature Versus Time



- Seepage possible after drift wall cools below boiling
  - Typically after ~ 1000 years
- Above ~110°C, only dust deliquescent environments possible

In-Drift Chemistry vs. Corrosion Testing Environments

Chemical Compositions of Principal Laboratory Testing Media

	J-13 Water	Basic Sat'd Water BSW-SC		Simulated Dilute Water		Simulated Concen'd Water		Simulated Acidified Water		Simulated Saturated Water	
		<110°C		60 and 90°C		60 and 90°C		60 and 90°C		100°C	
Ion	mg/L	mM	mg/L	mg/L	mM	mg/L	mM	mg/L	mM	mg/L	mM
K^+	5	2320	90,846	34	0.87	3,400	87	3,400	87	142,000	3,632
Na^+	46	10,059	231,224	409	17.8	40,900	1,780	37,690	1,780	487,000	21,182
Mg^{2+}	2	-	0	1	0.04	<1	20.04	1,000	41	0	0
Ca^{2+}	13	-	0	0.5	0.01	<1	20.01	1,000	25	0	0
F^-	2.2	85	1,616	14	0.74	1,400	74	0	0	0	0
Cl^-	7.1	5,000	177,695	67	1.89	6,700	189	24,250	684	128,000	3,610
NO_3^-	8.8	2,860	177,168	64	1.03	6,400	103	23,000	371	1,313,000	21,175
SO_4^-	18.4	176	16,907	167	1.74	16,700	174	38,600	396	0	0
HCO_3^-	129	1,786	107,171	947	15.52	70,000	1,148	0	0	0	0
Si(aq)	29	~251	7,059	27-49		27-49		27-49		-	
pH^-	7	12-13		9.8-10.2		9.8-10.2		2.7		5.5-7	
NO_3^-/Cl^-	0.55	0.572		0.545		0.545		0.542		5.87	

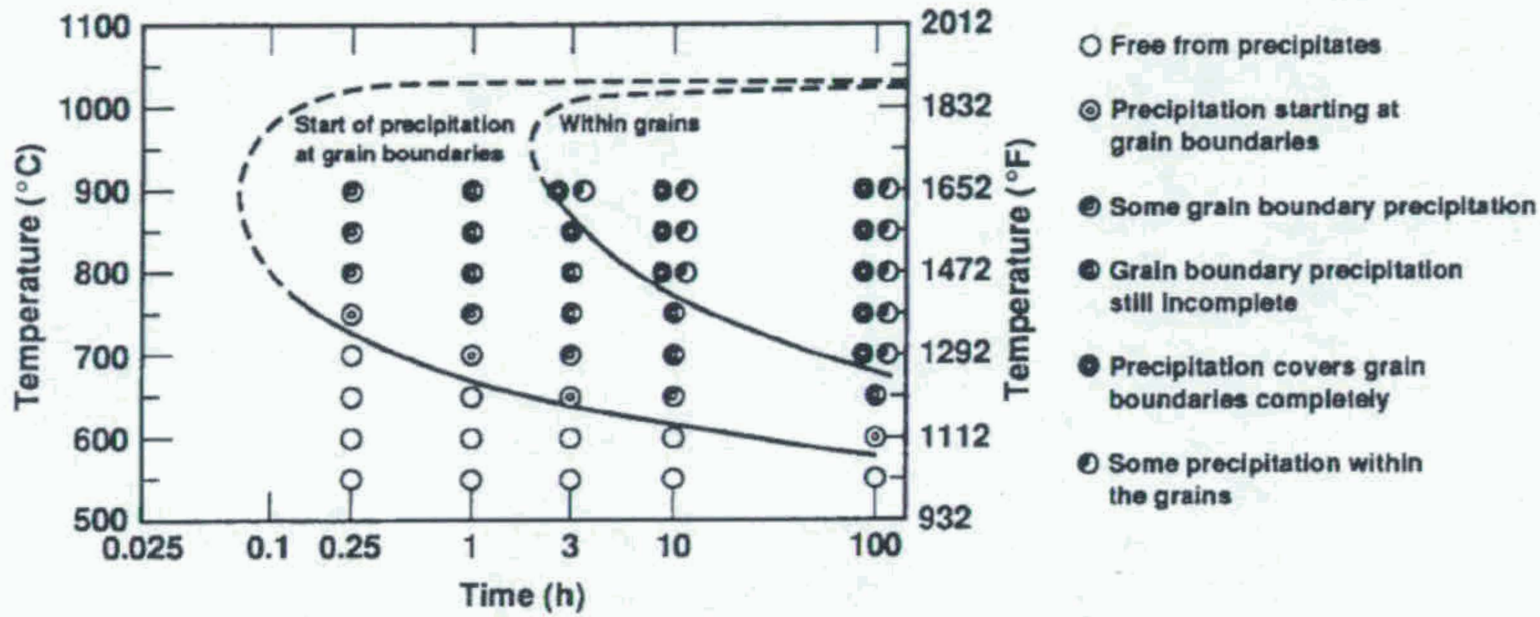
mg/L for test media from DTN:LL040803112251.117 and J-13 from DTN: MO0006J13WTRCM.000

- Principal testing media encompass
  - Concentrations from ~10 times J-13 to 45,000 times; pH from 2.7 to 12
  - F^- from 0 to 1,600 ppm ; Cl^- from 67 to 178,000 ppm
  - NO_3^- from 64 to 1, 300,000 ppm; NO_3^- / Cl^- from ~ 0.5 to 6
- Significant testing also performed in a broader range of seepage, pore water and deliquescent brine environments at temperatures to 220°C

Potential Degradation Modes

- Thermal aging
- Dry oxidation
- Hydrogen induced cracking (HIC)
- Microbiologically influenced corrosion (MIC)
- Effects of fluoride and bromide
- Corrosion under deliquescent dust
- General corrosion
- Localized corrosion
- Stress corrosion cracking
- Effect of gamma radiolysis

Thermal Aging of Alloy 22



- Aging can lead to precipitation and resultant degradation in mechanical and corrosion properties due to
  - Topologically close packed (TCP) intermetallic phases (i.e. μ, P and σ) are enriched in Mo, W and potentially Cr
  - $Ni_2(Cr, Mo)$ type long range ordering (LRO) below ~600°C

Alloy 22 Thermal Aging Overview

- Thermal aging has been modeled using Thermo-Calc and DICTRA software
  - Model predictions compared to experimental results to benchmark model for Alloy 22
- Model predictions extrapolated over time indicate both TCP and LRO are not issues under Yucca Mountain thermal conditions
- Current data indicate post-fabrication solution heat treatment & quenching do not result in unacceptable aging effects

Solution Heat Treatment of Alloy 22

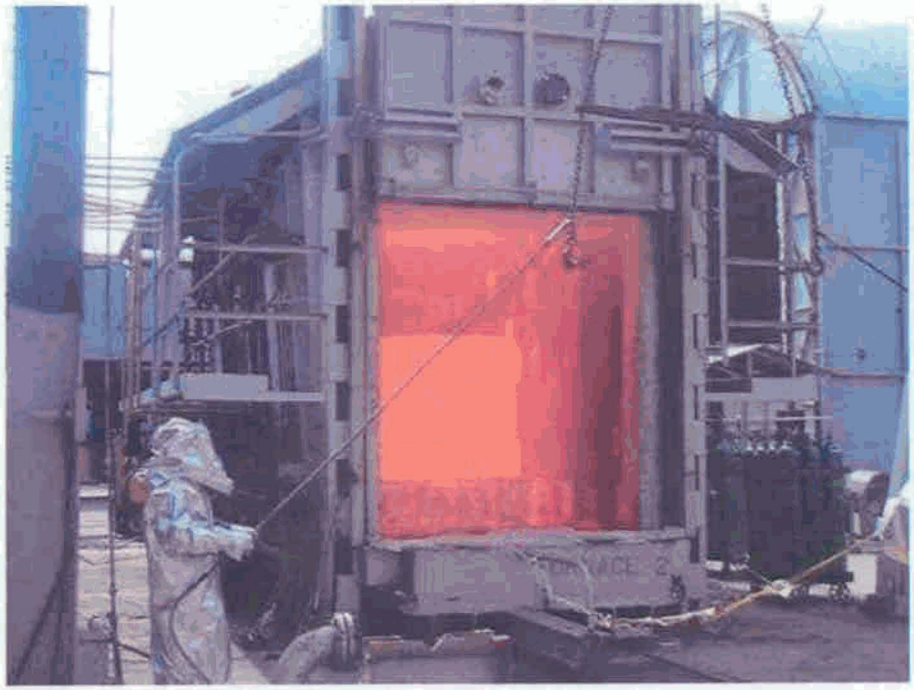
- **Alloy 22 waste package (WP) outer barrier solution heat treated following fabrication**
  - Fabrication specification states:

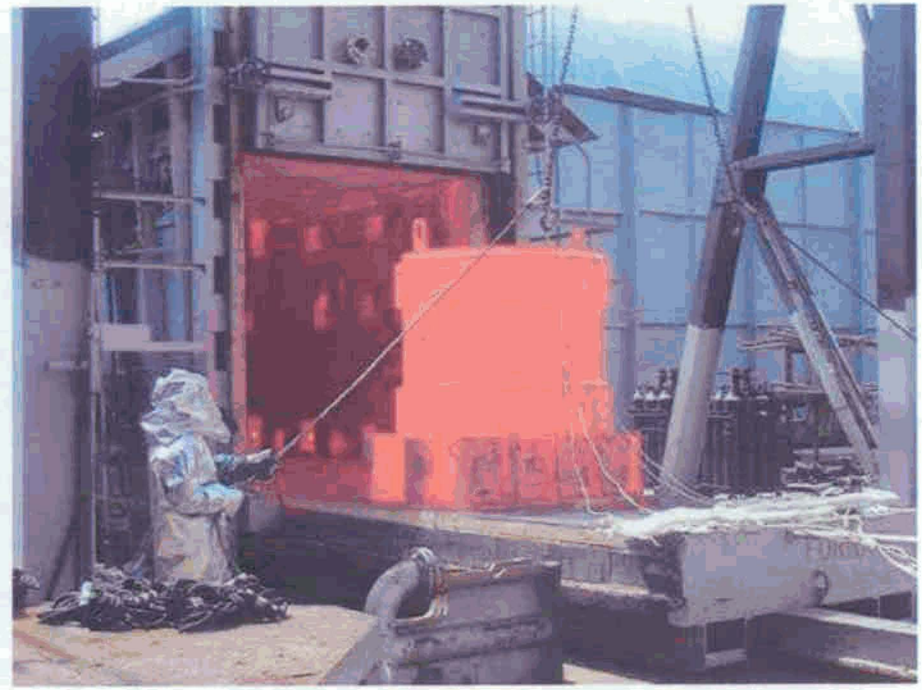
    "The Outer Corrosion Barrier shall be furnace heated at a soak temperature of 2050°F ± 50°F for 20 minutes minimum, after reaching temperature. Cooling will be achieved by immersion in water or spray quenching. Cooling rate for the entire outer shell shall be greater than 150°F/minute from soak temperature to below 700°F."

Solution Heat Treatment (SHT) of Alloy 22

- Full diameter, 1/4-length Alloy 22 WP outer barrier mockup fabricated in fiscal year 2000 (FY 00) to demonstrate fabricability and SHT feasibility
- Post fabrication solution heat treatment performed in vendor shop

Waste Package Mockup - Solution Anneal and Water Quench





Waste Package Mockup:

- Full-scale diameter, Quarter Length
- Material: Alloy 22
- Solution Anneal Temperature: 1150°C
- Heat Up Time: 3.5 hours
- Quenched in agitated water bath

Waste Package Mockup Thermocouples

Thermocouple Locations:

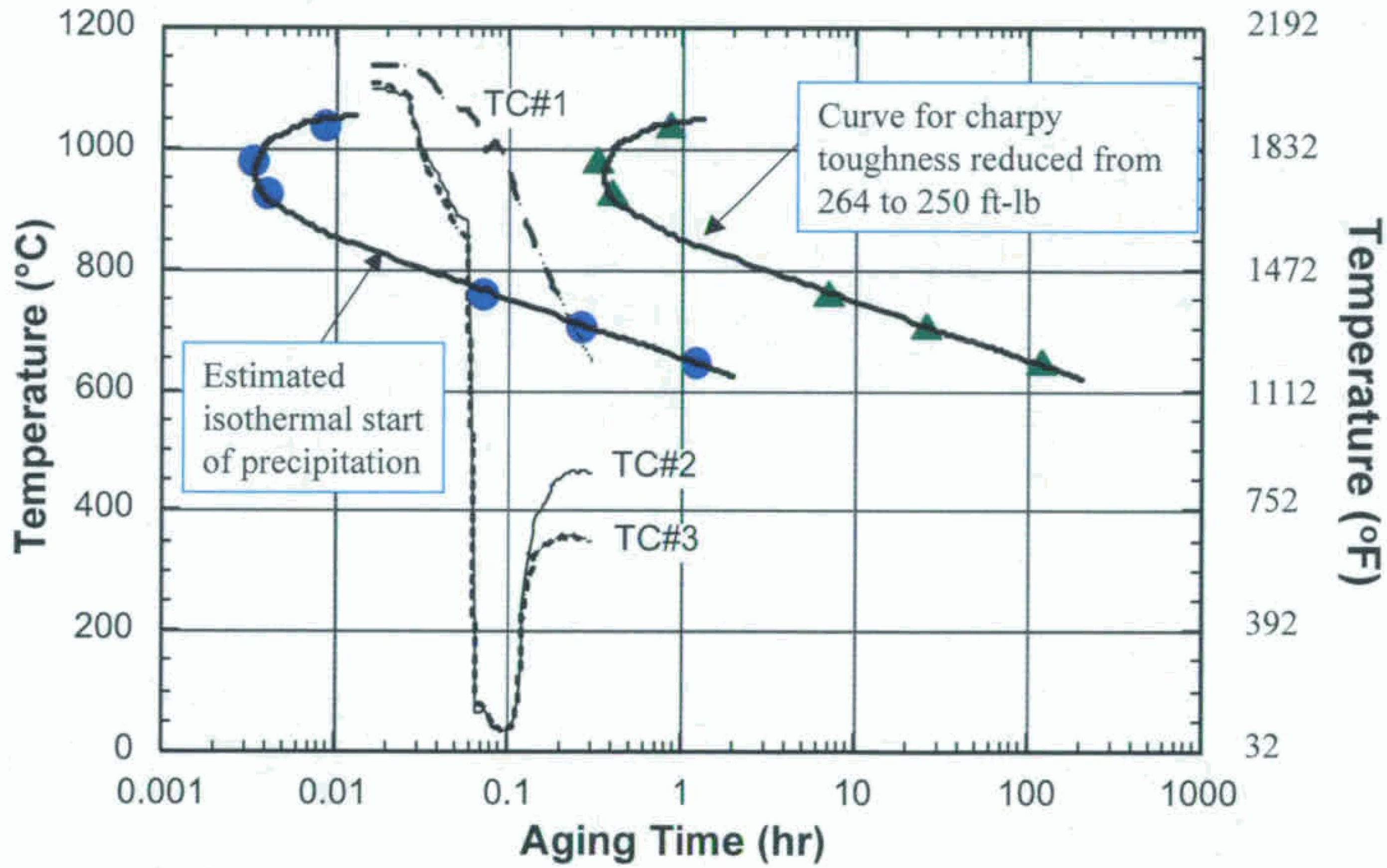
No. 1: Inner surface of shell, approx. 50 mm above internal support ring
No. 2: Outer surface of the bottom trunnion ring, approx. 75 mm below top of the ring
No. 3: Outer surface of the shell, midway between the trunnion rings

Waste Package Mockup in Quench Bath

- Close-up views of Waste Package Mockup fully immersed in water bath tank
- Approximately 17.5 minutes elapsed between furnace exit and removal from the water bath tank

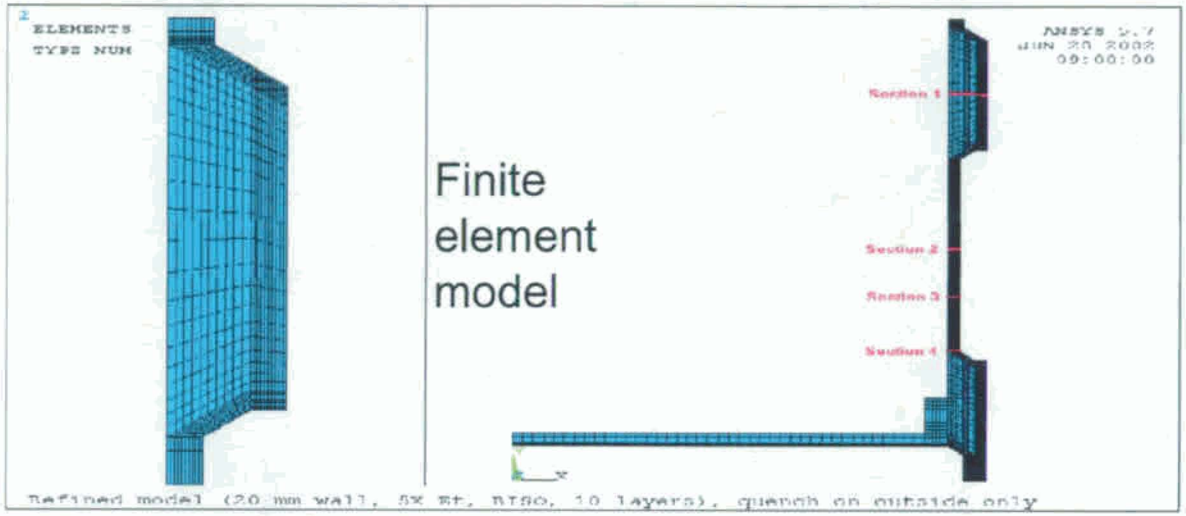
WP Mockup Cooling Response Relative to Alloy 22 TTT Curves

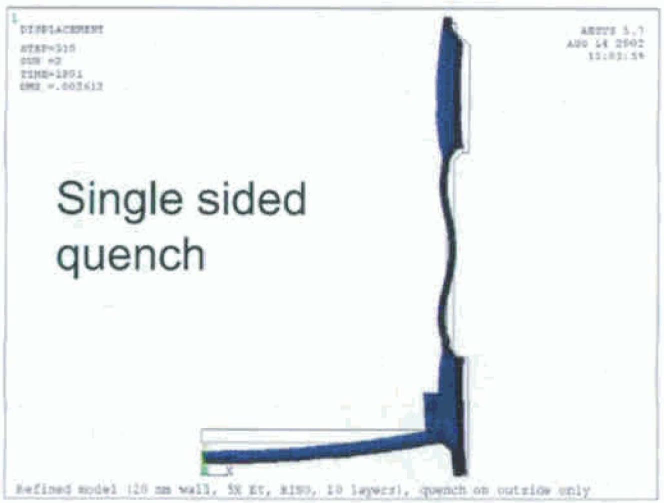
(Water quenched with no water inside. Container lifted out of water after 4.5 minutes and air cooled)

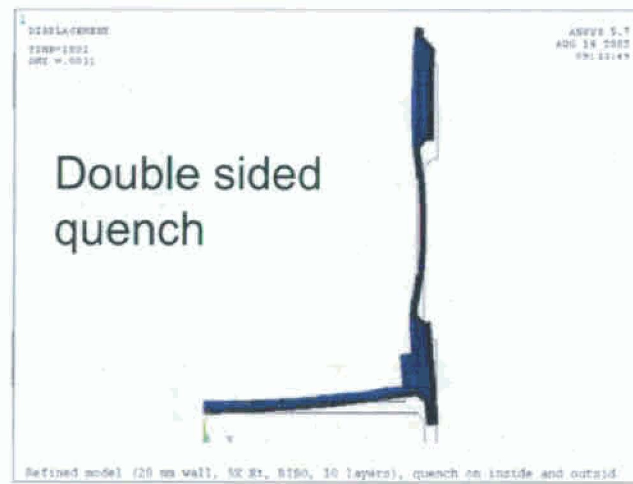


Outer surface quench rate met fabrication specification requirements

Stress Analysis* for One versus Two Sided Quench







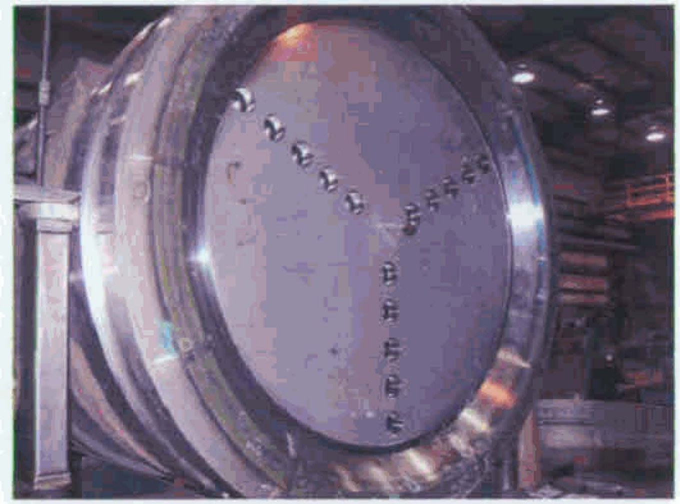
Double sided quench results in lower calculated peak outer surface stresses

*Analysis performed by Structural Integrity Associates for YMP

Mockup 'Hockey Puck' Evaluation Specimens

(used to evaluate microstructure and corrosion response)

TOP – AFTER SPECIMENS REMOVED



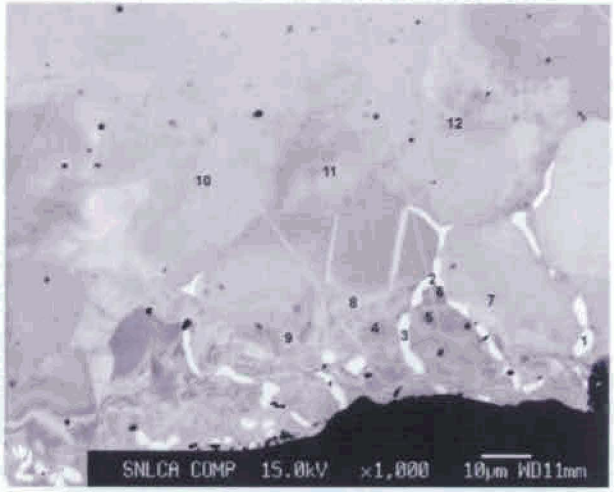
SPECIMEN NOTATION

Post-Annealing Evaluation

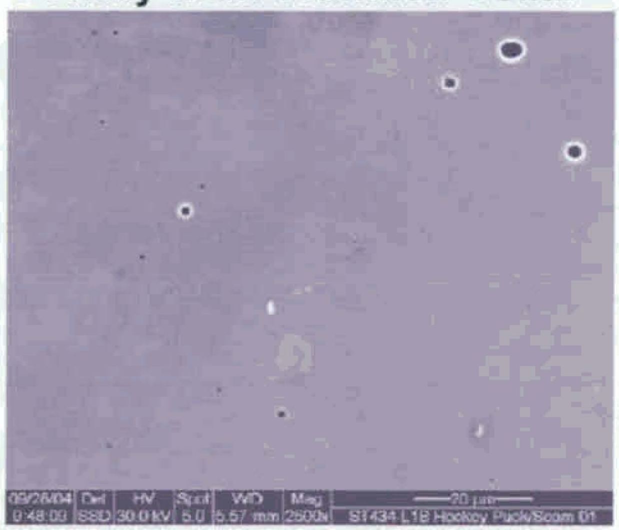
- “Hockey Puck specimens removed from solution heat treated/quenched, full-diameter Alloy 22 WP outer shell
  - Specimens subjected to detailed evaluation (weld seam and base metal) including
    - Metallographic and TEM examination
      - <0.05% Topologically Close Packed (TCP) phases remained in weld metal
      - Less than ~0.1% present before solution anneal

TEM Analysis of Mockup Seam Weld

Under Trunnion Collar



Away from Trunnion Collar



Wavelength Dispersive Spectroscopy

	Location	Elemental Weight Percent (%)				
		Cr	Mo	Ni	W	Total
	1	29.2	29.7	33.3	4.7	96.9
Precipitates	**2**	27.9	28.4	34.5	4.5	95.3
	3	28.2	29.0	34.5	4.6	96.3
	4	20.9	13.4	60.4	2.8	97.6
	5	20.2	12.6	62.0	2.8	97.5
	6	20.0	12.1	62.9	2.4	97.4
	7	21.3	13.5	60.7	2.7	98.2
Matrix	**8**	21.4	14.0	60.0	3.0	98.4
	9	20.9	13.9	60.6	3.0	98.5
	10	21.6	14.4	60.3	3.3	99.6
	11	21.8	14.1	60.3	2.9	99.1
	12	21.4	14.1	59.8	2.9	98.2

Typical Composition of TCP Phases (wt %)

Phase	Cr	Mo	Ni	W
σ	23	35	34	4.2
P	21	37	33	5
μ	20	39	33	6.3

Precipitates rich in Mo, W and Cr consistent with expected TCP phases

‘Hockey Puck’ Corrosion Evaluation

- General and Localized Corrosion Measurements Indicate
  - No effect of solution annealing on corrosion behavior (results described in Raul Rebak’s presentation)

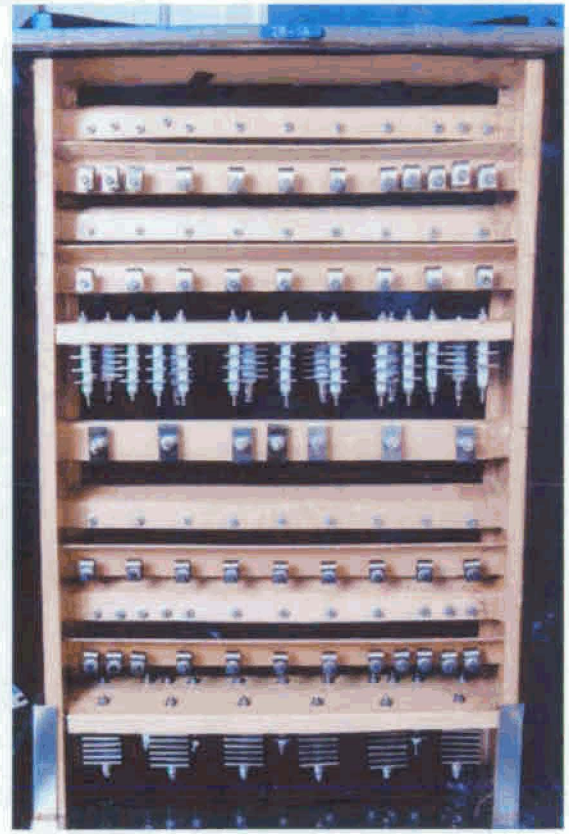
Potential Degradation Modes for Alloy 22

- **Dry oxidation:** Not a performance limiting process in the repository. (an oxide thickness of ~ 0.26 mm is predicted after an exposure of 10,000 years at 550°C).

- **HIC:** Fully annealed nickel-base alloys are essentially immune to HIC (even cold-worked to yield strength). Very low corrosion rate provides insufficient hydrogen.

General and Localized Corrosion
Long-Term Corrosion Test Facility (LTCTF)

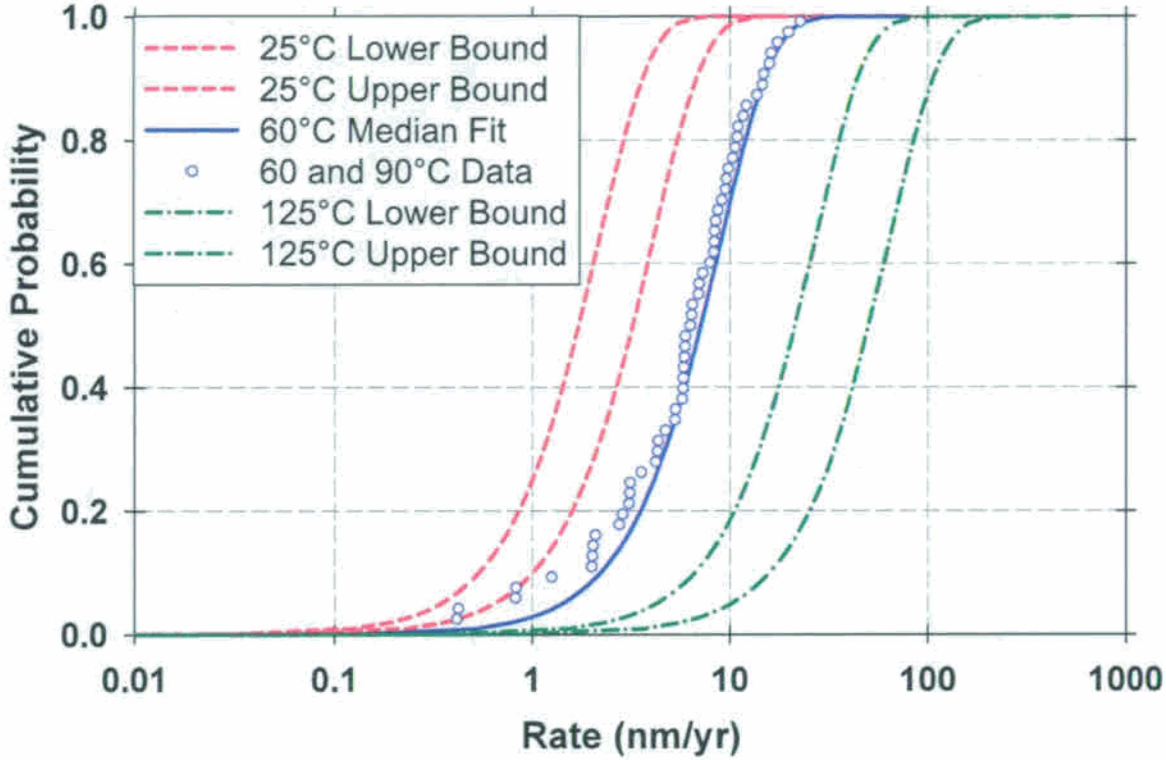
Test facility tanks



Test specimen rack

- Evaluation of general,localized, galvanic and stress corrosion
- Over 20,000 specimens on test

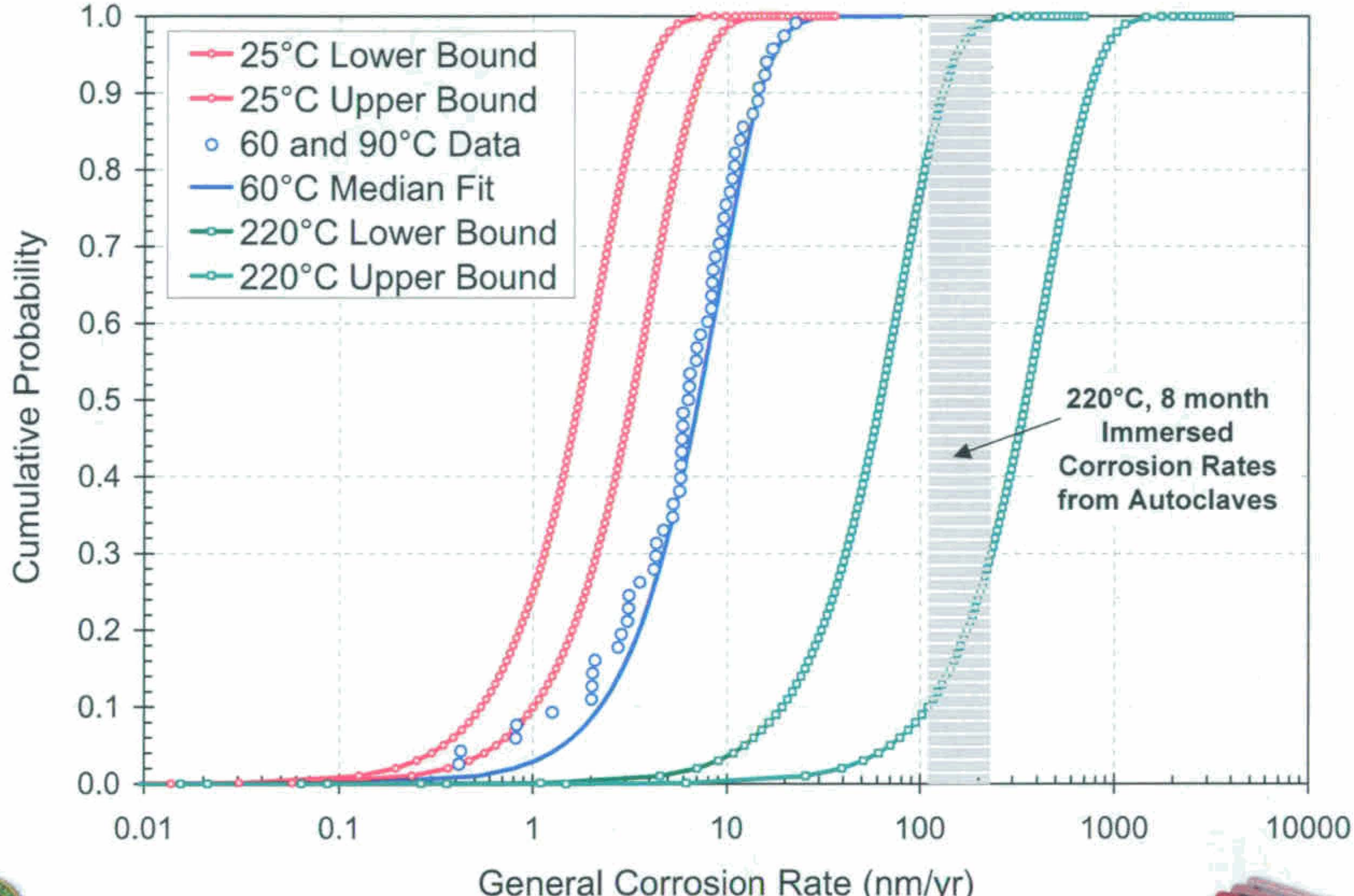
General Corrosion of Alloy 22



$$R = \exp\left[C_o - \frac{C_1}{T}\right]$$

- Rates from 5-year exposures in LTCTF. Confirmed over a range of environments and temperatures.
- C_o based on Weibull Distribution fit to long-term weight-loss data
  - Scale factor of 8.88 nm/yr and shape factor of 1.62
- C_1 = Truncated Normal Distribution
  - Mean activation energy = 25.91 kJ/mol

Autoclave Results Agree with General Corrosion Rate Model



Localized Corrosion (LC) Model

- Crevice repassivation potential (E_{rcrev}) used as critical potential for LC initiation

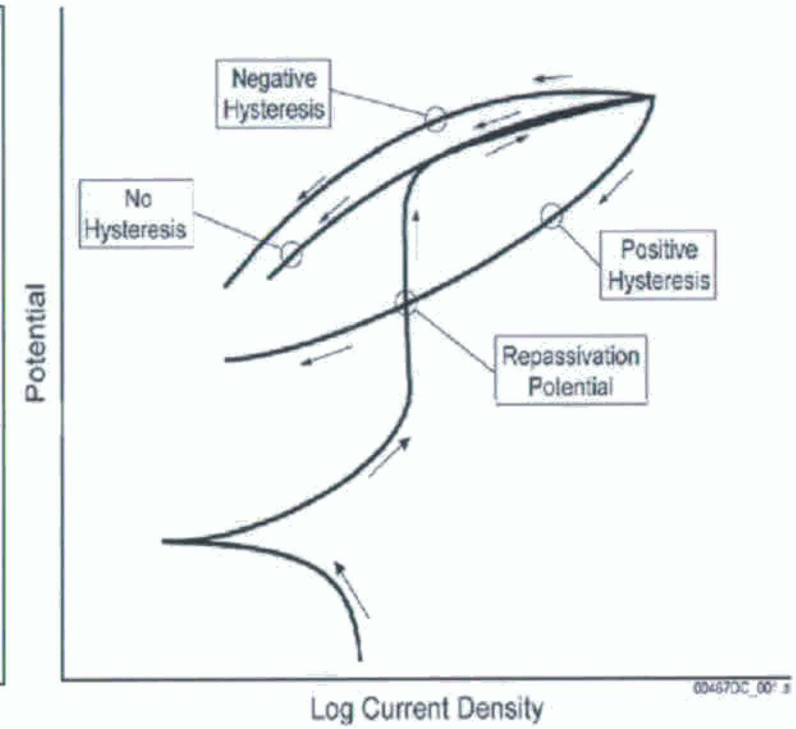
Initiation criterion: ΔE (= $E_{critical} - E_{corr}$) ≤ 0

$$E_{rcrev} = E^{o}_{rcrev} + \Delta E^{NO_3^-}_{rcrev}$$

$$E^{o}_{rcrev} = a_o + a_1 T + a_2 pH + a_3 \log([Cl^-]) + a_4 T \times \log([Cl^-])$$

$$\Delta E^{NO_3^-}_{rcrev} = b_o + b_1 [NO_3^-] + b_2 \frac{[NO_3^-]}{[Cl^-]}$$

$$E_{corr} = c_o + c_1 T + c_2 pH + c_3 [Cl^-] + c_4 \log\left(\frac{[NO_3^-]}{[Cl^-]}\right)$$

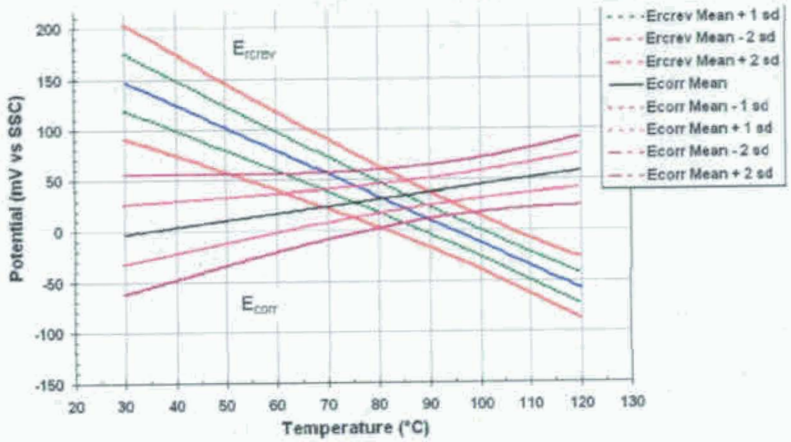


- ΔE is a function of T, pH, $[Cl^-]$, $[NO_3^-]$ and $[NO_3^-]/[Cl^-]$

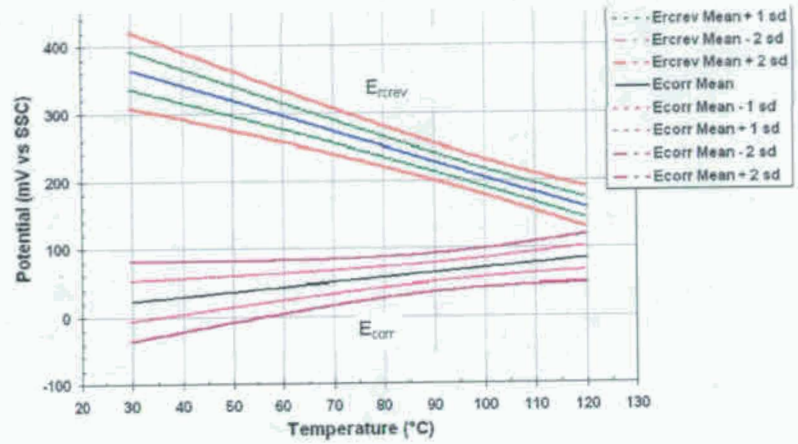
Degradation of Alloy 22 - Localized Corrosion Model

← Effect of $[NO_3^-]/[Cl^-]$ →

10 m Cl^-, pH 7, $[NO_3^-]/[Cl^-] = 0.05$

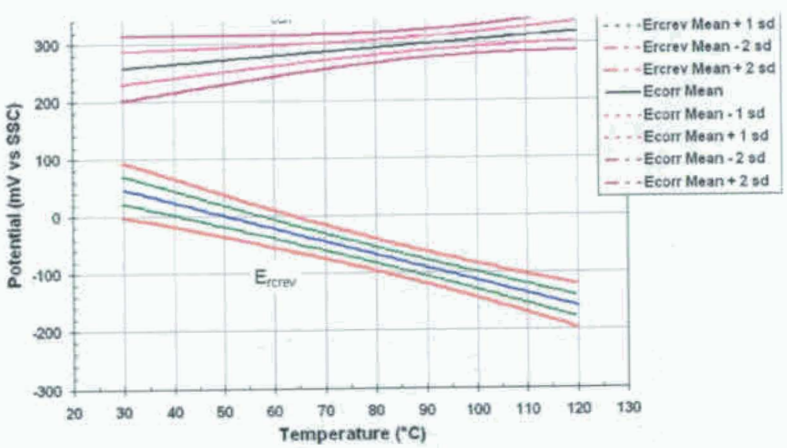


10 m Cl^-, pH 7, $[NO_3^-]/[Cl^-] = 0.25$

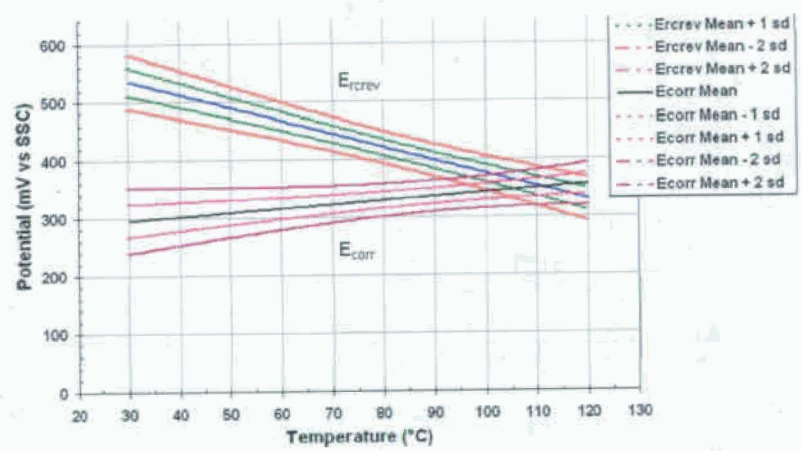


← Effect of pH →

10 m Cl^-, pH 3, $[NO_3^-]/[Cl^-] = 0.05$



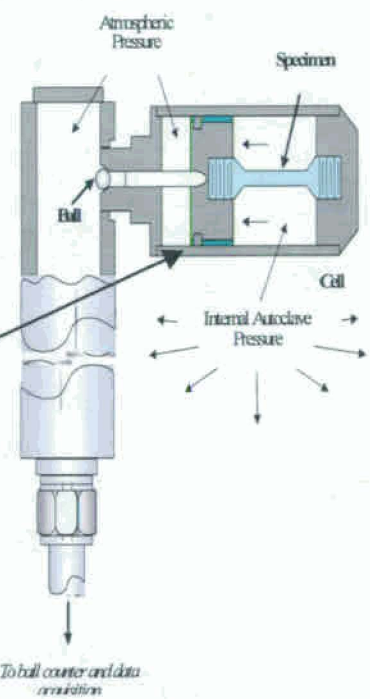
10 m Cl^-, pH 3, $[NO_3^-]/[Cl^-] = 0.50$



- LTCTF: No crevice corrosion in LTCTF at 60 and 90°C for 5 years
- CNWRA: No localized corrosion when $[NO_3^-]/[Cl^-] > 0.2$ in 0.5M NaCl at 95°C

Alloy 22 Stress Corrosion Cracking (SCC)

- SCC initiation observed in bicarbonate containing brines, but only under slow strain rate testing on anodically polarized ($E_{app} > E_{corr}$) specimens*
- However, no SCC initiation observed under constant load after 3 years exposure in 110°C BSW at stresses ≤ 96 % of ultimate tensile strength
  - Test conditions included mill annealed, as-welded, 20% cold worked and thermally aged (creviced and uncreviced)

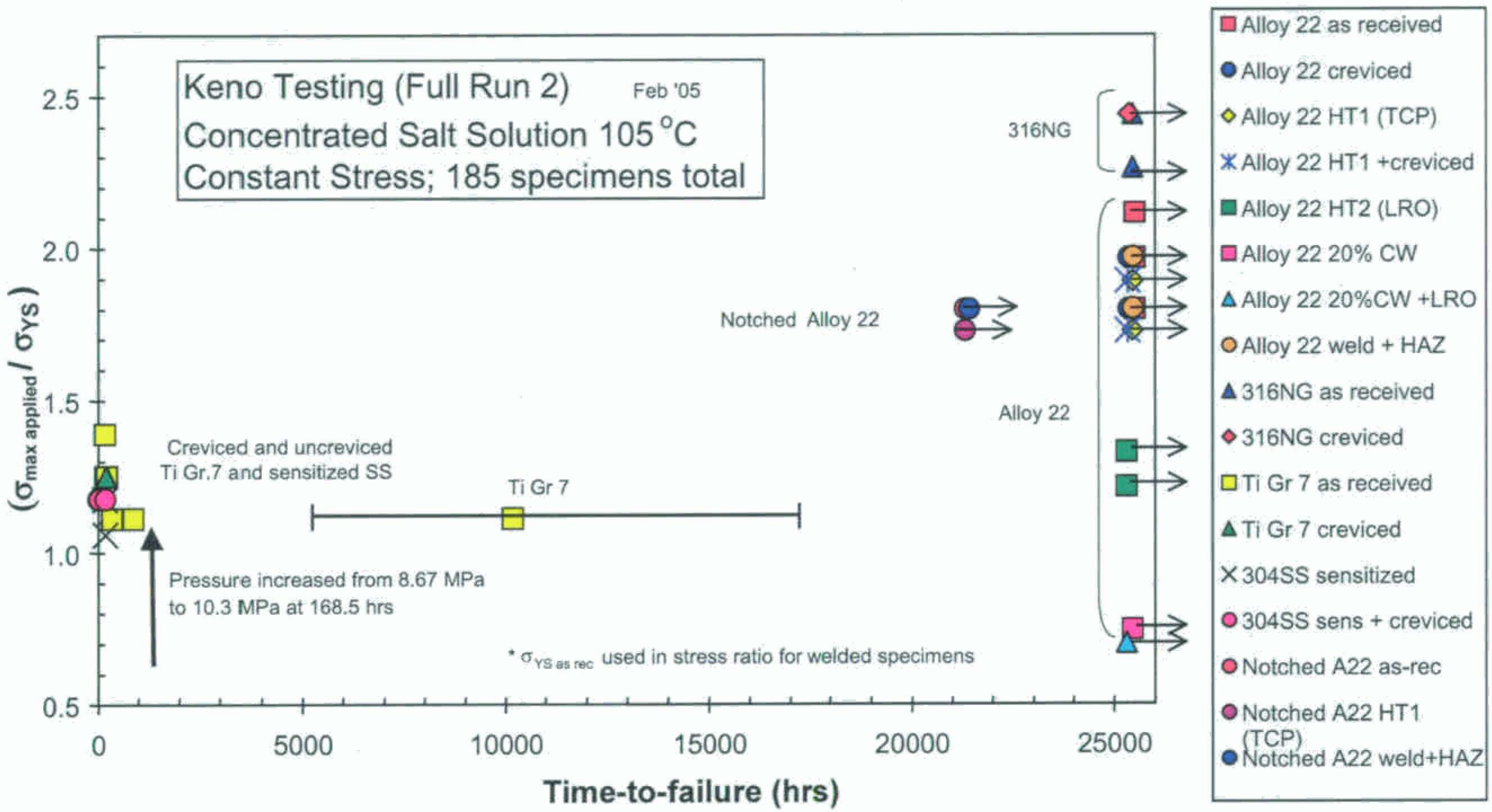


Constant Load (Keno) test module located in autoclave

King, et al., Paper No. 04548, Corrosion 2004, NACE

Shukla, et all., Paper No. 06502, Corrosion 2006, NACE

Constant Load SCC Initiation Results

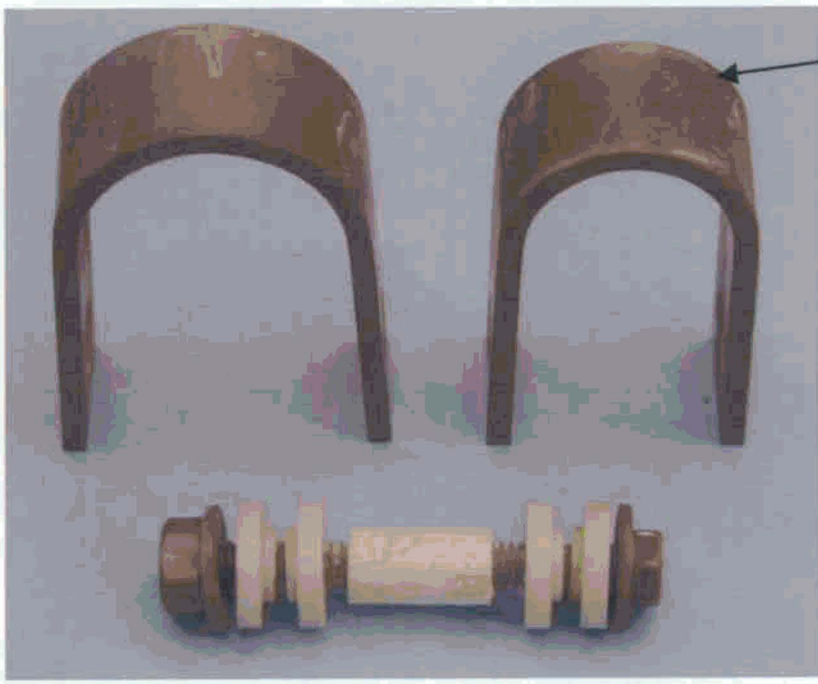


None of 120 Alloy 22 specimens have failed after 25,000 hours on test*

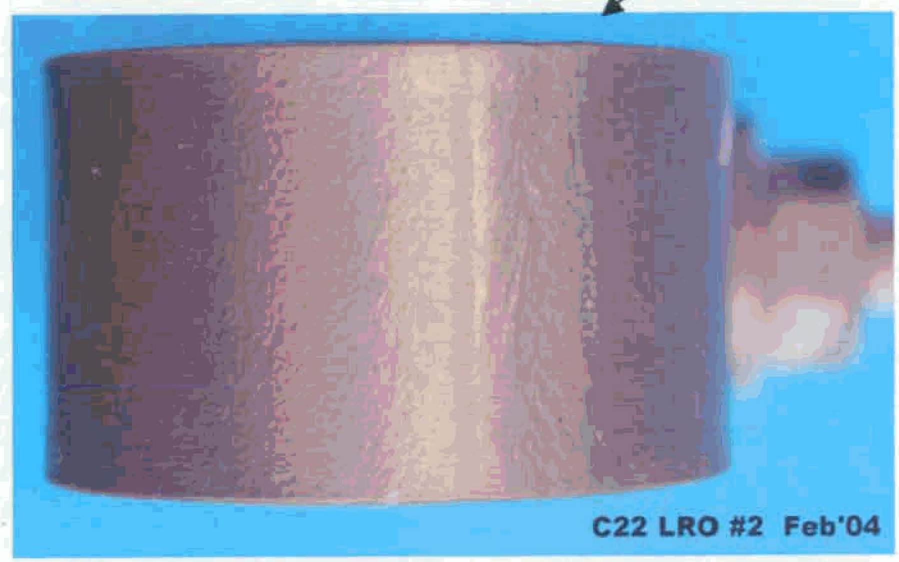
Andresen et al., 12th Int'l Conference on Environmental Degradation, Salt Lake City, August 14-18, 2005

Stress Corrosion Cracking (SCC)

- Also, no evidence of SCC initiation observed for Alloy 22 U-bend specimens exposed to a range of relevant environments
  - LTCTF after five years of exposure at 60 and 90°C
  - Autoclave tests (single and double U-bends) for 15,000 hrs in 165°C SCW

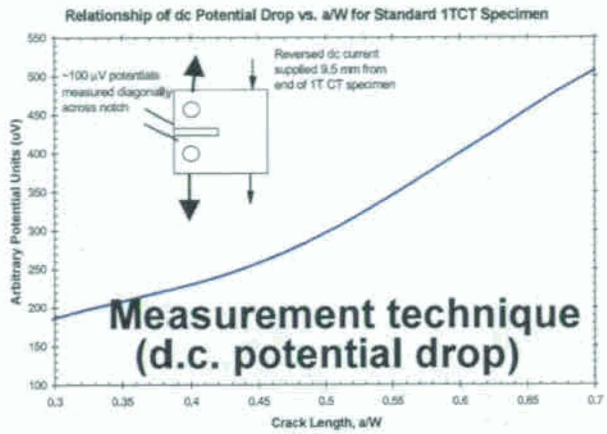


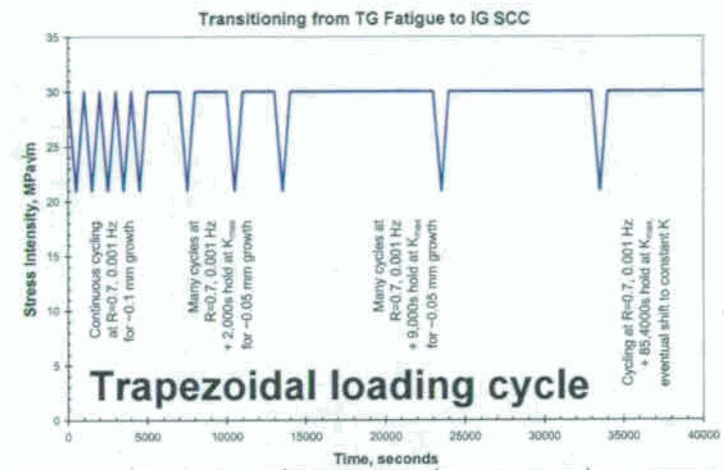
Disassembled Double U-bend



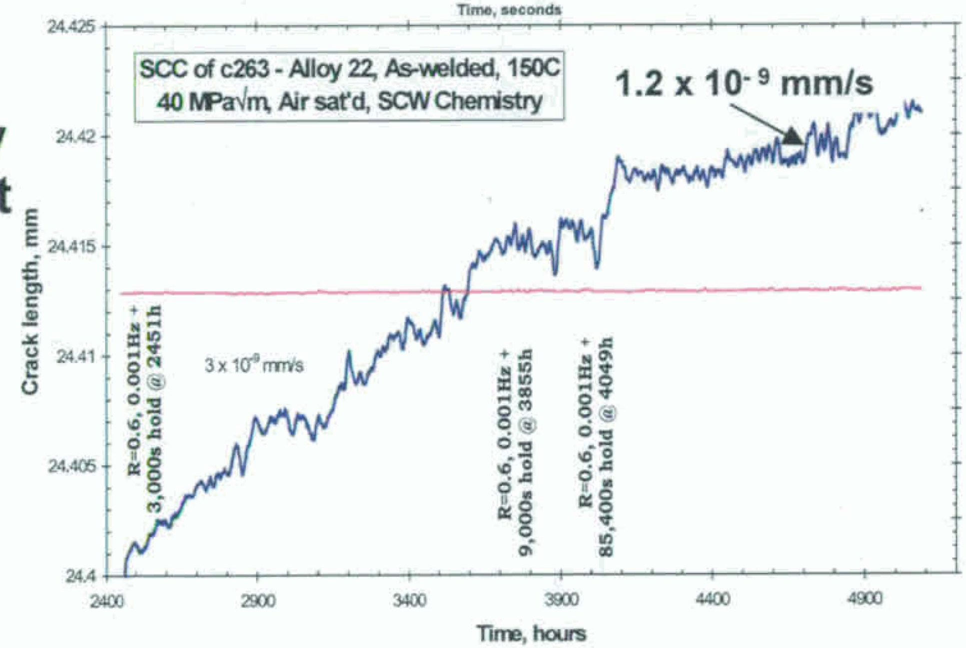
Apex of welded plus aged single U-bend

Alloy 22 SCC Growth





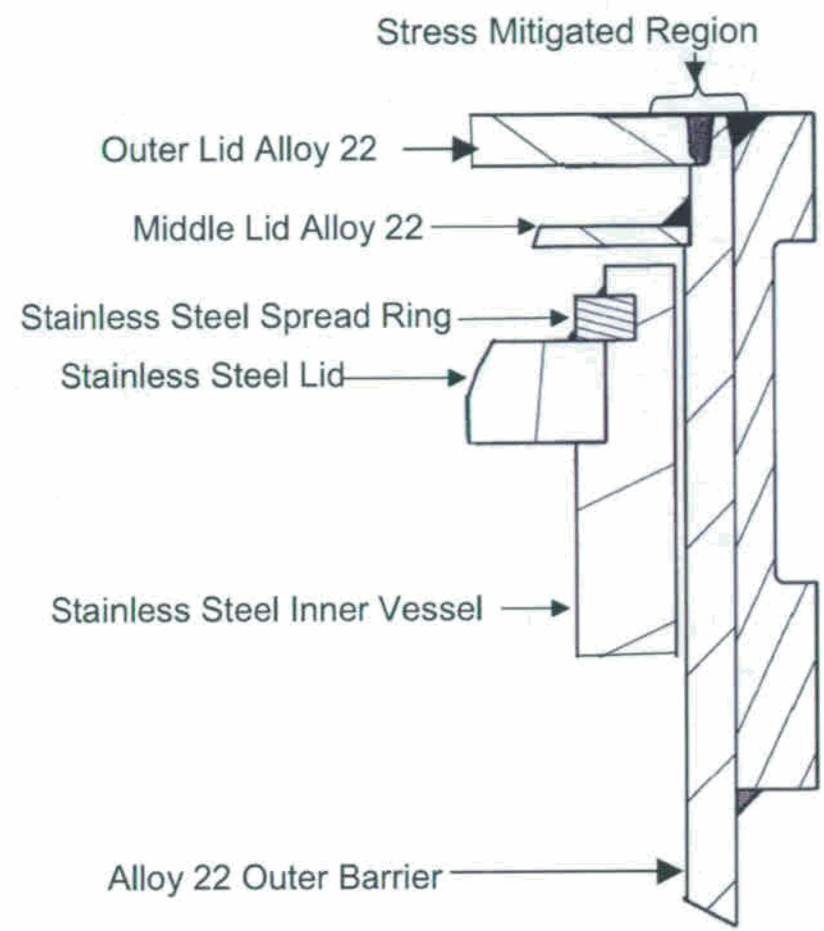
- Although Alloy 22 extremely resistant to SCC initiation, very slow crack growth can occur at flaws under sustained load
- Therefore, residual stress mitigation planned for final closure welds.



As-welded specimen exposed to 150°C SCW

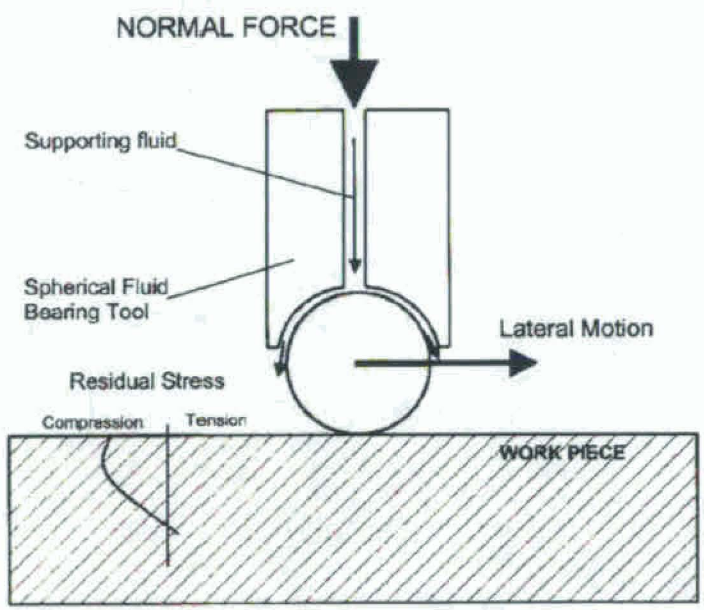
Alloy 22 (WP) Cross Section

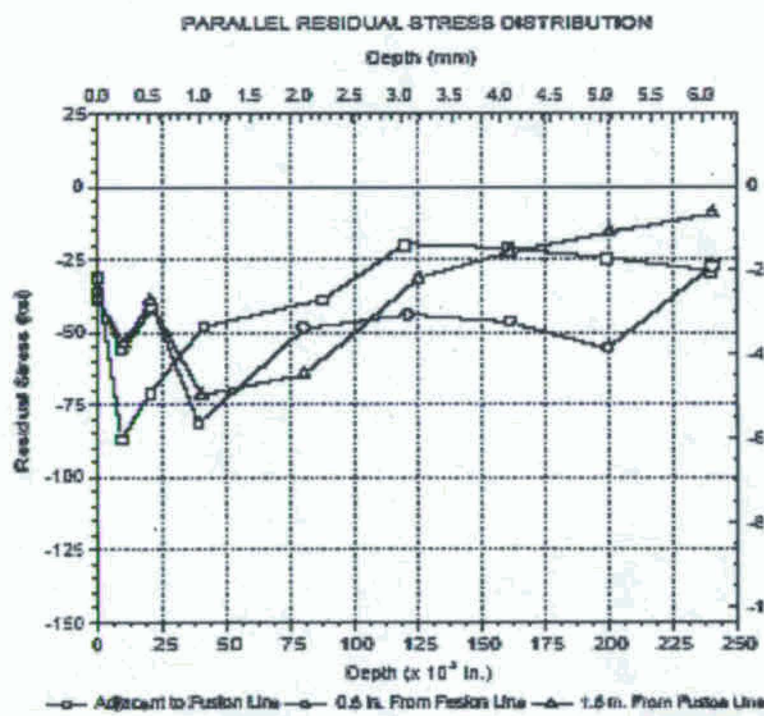
- Outer Alloy 22 barrier shell
  - Solution annealed after fabrication
- WP closure lid weld stress mitigated by plasticity burnishing
  - Delays onset of SCC
- Middle lid unmitigated
- No corrosion credit for stainless steel inner vessel



Plasticity Burnishing

- Value engineering study recommended plasticity burnishing with water supporting fluid
- Fast, simple, needs limited space and equipment





Degradation of Alloy 22 (continued)

- **MIC:** Resistant to MIC.

  Using f_{MIC} up to 2 in $CR_{MIC} = CR_{st} \cdot f_{MIC}$

- **Fluoride & bromide:** No pitting or crevice corrosion (LC) observed in 1 M NaF at pHs 6, 7.3 and 9 under mill annealed and thermally aged conditions (TCP and LRO).

  No LC in SCW - contains 1,400 mg/L fluorides.

  Similar results for 1M NaBr tested at pH 6.

- **Gamma irradiation:** In aggressive $MgCl_2$ brines, no enhancement of general corrosion and no pitting or crevice corrosion are observed in Alloy C-4 below approximately 100 rad/hr.

  For 21 PWR spent nuclear fuel assemblies, 1650 rad/hr (max) for the first 50 years when there is no water and < 100 rad/hr after 50 years.

Conclusions

- General corrosion rates low
- Localized corrosion unlikely in neutral pH nitrate-containing chloride solutions
- Stress corrosion cracking in closure weld regions only
  - Shell annealed before emplacement
  - Outer lid closure weld laser peened

Based on literature, extensive testing results and modeling projections, Alloy 22 WP is highly resistant to the full range of anticipated degradation modes evaluated.


Questions?

Canistered Fuel Option Under Consideration

- Utilities load fuel into Transport, Aging and Disposal Canisters (TADs) which are shipped to YMP in shielded transport containers
- TADs loaded into waste packages
  - Minimizing handling of bare fuel.
- The outer Alloy 22 WP lid(s) would then be weld sealed.